NO_x REDUCTION IN PULVERIZED COAL COMBUSTORS USING WASTE COAL AS COAL-WATER SLURRY

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INTRODUCTION

In order to comply with the regulations for nitrogen oxides emissions, various abatement strategies have been developed. These strategies can be divided into the following categories: 1) modification of the combustion configuration, 2) injection of reduction agents into the flue gases, and 3) treatment of the flue gas by post-combustion de-nitrification processes. A determination of the most effective and least expensive abatement technique depends on specific boiler firing conditions and the emission standards. A combination of techniques may be necessary to achieve certain mandated limits. Hence, the best NO_x control strategy for a certain unit is highly site dependent.

No definite rules exist to determine which nitrogen oxide formation mechanism dominates for a given stationary combustor configuration because of the complex interactions between burner acrodynamics, and both fuel oxidation and nitrogen species chemistry. But in general, fuel nitrogen has been shown to dominate pulverized coal fired boilers, although thermal NO is also important in the post-flame regions where over-fire air is used. Pershing and Wendt [1] showed that thermal NO contributions only become significant at temperatures above 2,500 °F in coal flames. Prompt NO] is not a major source during coal combustion. Coal-water slurry (CWS) prepared from waste coal has a potential to reduce NO_x emissions [2, 3]. Reburning is proposed as a general mechanism for lower NO_x emissions when cofiring coal-water slurry with PC [3]. Coal-water slurry reburning is applicable to all types of coal-fired boilers and offers electric utilities a potential option to achieve significant NO_x emissions reduction [4].

OBJECTIVES

The main objective of this study was to gain insight into the mechanism by which NO, emissions are lowered when cofiring coal and CWS as compared to coal firing by examining the extent of reburning in the gas phase, and understanding the heterogeneous char NO contribution to the reduction of NO.

EXPERIMENTAL

The study was conducted in the 0.5 MMBtu/h Down fired combustor (DFC) located at the Energy Institute of Penn State. Figure 1 provides a schematic diagram of the 0.5 MMBtu/h DFC. Detailed description of the facility can be found elsewhere [5]. Coal was fired through the central pipe of the burner, and slurry fuel was injected in Port 2 to simulate the reburn conditions. CWS was cofired with coal at 0, 10, 20, and 30 % of the total thermal input. A total of fifteen tests were performed in the DFC. Compositional analysis of the coal and CWS are provided in Table 1. Baseline flue gas concentration and temperature profile along the combustor was obtained when firing 100% coal. A continuous emission monitoring (CEM) system was used to measure O_2, NO, and CO at various Port levels. Axial oxygen concentration measurement was also obtained.

Table 1. Compositional analysis (wt%, dry basis) of PC and CWS

Fuel	Fixed Carbon	Volatile Matter	Ash	HHV (Btu/lb	C	H	N	S	O
Coal	62.94	24.17	12.89	13,339	76.10	4.66	1.37	1.59	3.39
CWS	60.06	30.29	9.65	13,353	77.07	4.51	1.34	1.32	6.11

A nominal firing rate of approximately 0.5 MMBtu/hr was used in the study. Ports were installed as per EPA methods for stack gas sampling for the sulfur oxides evaluation. The coal-water slurry fuel atomization gun was placed at Port 2 for all tests. Combustion air for coal-water slurry fuel during all reburn tests was introduced in Port 3 of the DFC. An air pressure of 100 psig was used for atomizing the CWS.
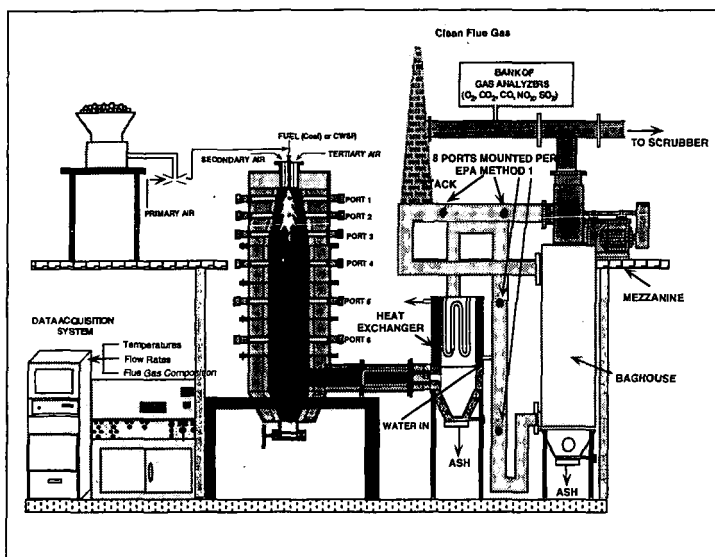
Figure 1. Schematic diagram of the down fired combustor (DFC).

Data on the gas temperatures using LAND suction pyrometer, and oxygen, CO, and NO_x concentration profiles using continuous emission monitoring system (CEM) in the combustor were also obtained during the tests. Char samples were collected from various Ports in the DFC using an isokinetic sampling probe. The char samples were collected in wet condition by washing the probe after each test and were analyzed for carbon, hydrogen, nitrogen, and carbon burnout.

RESULTS AND DISCUSSION

The gas composition (O_2, CO and NO_x) at various Port levels was measured at the center of the combustor, midway between the center and the wall (called "Mid") and at the wall. The results, when firing 100% PC with all the air though the burner (Figure 2), show that the NO_x concentration in the gas phase was maximum near the burner and as the flue gases pass down the combustor, the NO_x levels decrease. Thi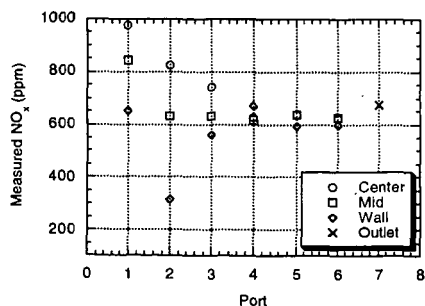s suggests that the rate of destruction exceeded the rate of production of NO_x. This increase in the destruction is possibly accomplished by the reburn mechanism. Reburning can take place either by homogeneous gas phase reactions or by the NO_x - char reactions. Upon heating a coal particle, nitrogen is also distributed between the volatile and char phases. NH_l and HCN species in the volatiles depending on the temperature, concentration and mixing can form NO_x or N_2. Simultaneously the char nitrogen will be released to form either NO_x or finally to N_2. Depending on the

Figure 2. NO_x Profile in the DFC when firing 100% coal with all the air through the burner

net difference between the two processes, an increase or a decrease in the NO_x emissions occurs. It can be seen from Figure 3 that the init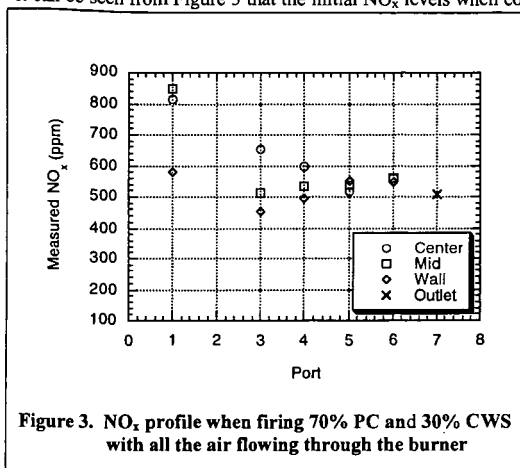ial NO_x levels when cofiring coal-water slurry are lower than the values for 100% PC. This suggests that the formation of NO_x in the initial phases is lower. Subsequently there is a minor decrease in the NO_x concentration for the tests with CWS cofiring tests. These results indicate that the NO_x production and destruction rates after the primary zone are almost equal leading to no net increase in NO_x levels. Conceptually, the reburning process can be divided into three zones: a) Primary Combustion Zone: This is the main heat release zone which accounts for approximately 80 % of the total heat input to the system and is operated under fuel-lean conditions. The level of NO_x exiting this zone is defined to be the input to the reburning process; b) Reburning Zone: The reburning fuel (10-30 % of the total fuel input) is injected downstream of the primary zone to create a fuel-rich, NO_x reduction zone. Reactive nitrogen enters this zone from two sources: the primary NO_x input and the fuel nitrogen in the reburning fuel. These reactive nitrogen species react with hydrocarbon radicals, primarily CH, from the reburning fuel, to produce intermediate species like NH_3 and HCN [6]. The HCN then decays through several reaction intermediates and ultimately reaches N_2; c) Burnout Zone: In this final zone, air is added to produce overall lean conditions and oxidize all remaining fuel fragments. The total fixed nitrogen species (TFN = NH_3 + HCN + NO + Char N) will either be oxidized to NO_x, or reduced to molecular nitrogen.

Figure 3. NO_x profile when firing 70% PC and 30% CWS with all the air flowing through the burner

The amount of nitrogen from the fuel into volatiles and char will change as a function of temperature, nitrogen content and size of the coal particle. Figure 4 shows the wall temperature profiles for various cofiring configurations. A test was performed with 100% PC but water, equivalent to 30% CWS test, injected in Port 3 to separate the effect of NO_x changes due to temperature decrease and any re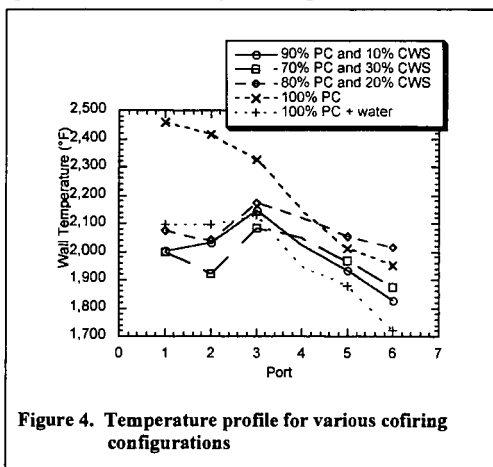burning reactions. Since all the fuel and combustion air was admitted through the burner the resulting temperature in the case of 100% PC was higher than the rest of the tests. This contributes to higher thermal and fuel NO_x during primary combustion zone. Partitioning of nitrogen between volatile and char phase is a function of temperature, heating rate and coal type and equipment used. It has been shown in the literature that total volatile and nitrogen yields are approximately proportional at comparatively low pyrolysis temperatures (1800 °F) and short heating times, but pyrolysis at temperatures > 2500 °F, results in the

Figure 4. Temperature profile for various cofiring configurations

evolution of significant amount of additional nitrogen [7]. Since the temperature for 100% PC in the Port 1 region is high (>2500 °F), it is likely that more nitrogen is released into gas phase which, with more air tends to form higher amounts of NO_x and thereby higher concentration of NO_x. However, there is a reduction in NO_x concentration between Ports 1 and 3. This is primarily due to gas phase reaction involving hydrocarbon species from the volatiles.

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Carbon burnout data as a function of distance from the burner was obtained from the isokinetic char samples that were collected during the tests. The data show that that the carbon burnout during cofiring runs was lower than that of 100% PC run. As a result, lesser amount of carbon was available in the form of HC radicals during the initial stages of cofiring than the 100% PC run. From Figure 5, it can be seen that the chars collected show higher amounts of carbon, and up to 18% of total nitrogen remaining in the char phase at Port 3. Wendt [8] has shown that under rich conditions, HCN plays a critical role in driving the nitrogen cycle to form N_2 and that one source of HCN formation is the destruc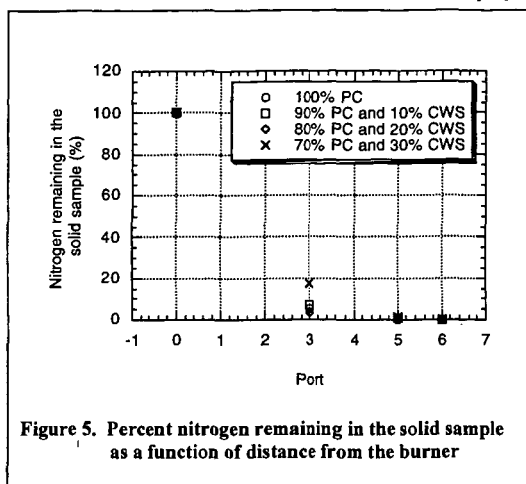tion of NO by hydrocarbon radicals, which is the main reburning reaction destroying NO. In addition, it has been shown [6, 9] that the Fenimore N_2 fixation reaction also produces HCN, especially under natural gas reburning conditions. Mereb and Wendt [10] confirmed the fact that reburning with pulverized coal is also effective but less than with gas because natural gas produces more hydrocarbon species in the NO_x reduction zone and reactions between NO and hydrocarbons are important. Their data showed that with coal reburning, HCN was destroyed more rapidly than it was being formed and its values decayed to levels below 20 ppm within 0.6 seconds. This result supported their hypothesis that it is important to maintain HCN formation rates during long time scales in order to keep N_2 formation mechanisms going, that this formation is mostly due to hydrocarbon reactions with NO or N_2 and that any slow release of nitrogen from the coal residue is a minor contributor to the process. The results in this study also confirm these observations since the residence time between Ports 1-4 is approximately 0.6-0.7 seconds. The gas phase reburning after this Port appears to be insignificant.

Figure 5. Percent nitrogen remaining in the solid sample as a function of distance from the burner

NO is expected to be the primary product of char nitrogen combustion [11]. However, the NO-carbon reaction can reduce the NO to N_2. NO reduction is enhanced by the presence of CO [11]. From the CO measurements in the combustor in this study, no significant difference in the CO in the gas phase emissions was observed. In most of the tests the CO concentration was around 100-120 ppm. Therefore, it is likely that the NO produced from oxidation of char nitrogen reacts with the carbon in the pore structure. Char produced from the coal-water slurry is texturally different from the char from PC combustion [12]. Therefore, local NO-char reactions are believed to be responsible for the small reduction in NO above and beyond the reduction obtained due to temperature reduction caused by water addition.

It was also seen from the data that there was a significant difference between the NO_x concentrations measured at the center and the wall. This indicates the lack of mixing in the combustor up to about 7-8 feet in the combustor. If the NO_x molecules do not mix with hydrocarbon radicals, the reduction in NO_x will be reduced. It has been shown [9] that the reburning mechanisms occur in two regimes: one in which fast reactions between NO and hydrocarbons are usually limited by mixing; the other in which reactions have slowed and in which known gas phase chemistry controls.

CONCLUSIONS

The results of the study showed that NO_x formation occurs during initial phases in the pulverized coal flames. The NO_x concentration profile indicated that the concentration decreases rapidly by reburning in the gas phase by the radicals in the volatile phase. Excess air levels (air staging), and mixing appeared to be the most important parameters in reducing the NO_x in the primary zone. When coal-water slurry was cofired with coal the temperature in the upper part of the combustor was lower because of water addition. The NO_x concentration near the Port 1 region of the combustor was also lower. This reduction was attributed to the lower temperature and lower fuel nitrogen split into the gas phase. The reduction of NO_x due to reburn in the primary zone was not observed for coal-water slurry cofiring tests. The carbon burnout was lower for the CWS cofiring tests. Therefore, lower amount of carbon was available in the volatile phase to

reduce NO_x initially. It is believed that gas phase reactions did not play a significant role in the reduction of gas phase NO_x that was produced initially.

Char contained higher amounts of nitrogen because of the char structural differences, the nitrogen oxides that are formed are believed to react on the char surface on their way out through the pore structure.

ACKNOWLEDGEMENTS

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